



Region 2
UNIVERSITY TRANSPORTATION RESEARCH CENTER

Final Report

Development of Highly Sensitive Portable Hydrocarbon Sensors

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16. Abstract A detailed investigation was performed on developing highly sensitive and portable hydrocarbon sensors using tailored quantum dot materials. These studies focused on using an Ocean Optics fiber optics based spectrometer for monitoring quantum dot arrays to detect the hydrocarbon targets. Studies were performed to determine the viability of using arrays for these studies, tailoring the quantum dot materials for higher sensitivity through energy transfer mechanisms, and tailoring the materials for enhanced stability. These studies showed that monitoring quantum dot arrays using a portable spectrometer, while a viable method, requires the reliable synthesis and subsequent reliable stability of the quantum dots. While CdSe quantum dots with tailored surface ligands were shown to be able to detect hydrocarbons with a 15ppm detection limit, the repeated synthesis and stability studies determined that these quantum dots suffer from reliability issues on both counts, which inhibited their use in long term development studies. In the absence of stable quantum dots, a study was performed which utilized ZnS capped CdSe quantum dots. These studies have proven that even without surface tailored ligands, hydrocarbons were detected within a 15-9400 ppm detection range, and moreso they showed stability over an 8 month time period. These were significant improvements obtained in these studies. It is expected that through the use of these more stable quantum dots and their enhanced films, developments involving tailored surface ligands and array studies that the detection limits could be enhanced into the ppb range. A detailed study on the surface ligand length dependence was also performed and it is expected that this benchmark study will enable future developments into energy transfer enabled sensing mechanisms. In summary, while material stability issues limited the full range of studies undertaken within this program, significant improvements were made in the knowledge of array studies using fiber optic based spectrometers, quantum dot material improvements for greatly enhanced reliability, and material studies which are fundamental for the study of future energy transfer mechanisms. With these significant gains, future studies aimed at quantum dot based hydrocarbon sensors will be enabled to improve the detection limits and the reliability of these methods. The work completed in this program has resulted in a manuscript submitted to the Journal of Physical Chemistry C and a manuscript submitted to the Applied Physics Letters journal. Furthermore, two students have graduated with their M.S. degrees during the time of this program.					
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Final Report

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Summary

A detailed investigation was performed on developing highly sensitive and portable hydrocarbon sensors using tailored quantum dot materials. These studies focused on using an Ocean Optics fiber optics based spectrometer for monitoring quantum dot arrays to detect the hydrocarbon targets. Studies were performed to determine the viability of using arrays for these studies, tailoring the quantum dot materials for higher sensitivity through energy transfer mechanisms, and tailoring the materials for enhanced stability. These studies showed that monitoring quantum dot arrays using a portable spectrometer, while a viable method, requires the reliable synthesis and subsequent reliable stability of the quantum dots. While CdSe quantum dots with tailored surface ligands were shown to be able to detect hydrocarbons with a 15ppm detection limit, the repeated synthesis and stability studies determined that these quantum dots suffer from reliability issues on both counts, which inhibited their use in long term development studies. In the absence of stable quantum dots, a study was performed which utilized ZnS capped CdSe quantum dots. These studies have proven that even without surface tailored ligands, hydrocarbons were detected within a 15-9400 ppm detection range, and moreover they showed stability over an 8 month time period. These were significant improvements obtained in these studies. It is expected that through the use of these more stable quantum dots and their enhanced films, developments involving tailored surface ligands and array studies that the detection limits could be enhanced into the ppb range. A detailed study on the surface ligand length dependence was also performed and it is expected that this benchmark study will enable future developments into energy transfer enabled sensing mechanisms. In summary, while material stability issues limited the full range of studies undertaken within this program, significant improvements were made in the knowledge of array studies using fiber optic based spectrometers, quantum dot material improvements for greatly enhanced reliability, and material studies which are fundamental for the study of future energy transfer mechanisms. With these significant gains, future studies aimed at quantum dot based hydrocarbon sensors will be enabled to improve the detection limits and the reliability of these methods. The work completed in this program has resulted in a manuscript submitted to the Journal of Physical Chemistry C and a manuscript submitted to the Applied Physics Letters journal. Furthermore, two students have graduated with their M.S. degrees during the time of this program.

Introduction

The testing of soil samples is performed during all phases of DOT related construction (planning, building, and post construction). This is done to ensure that the soil removed is not contaminated and when construction is complete to ensure that the environmental impact of the structure is minimized. NYS-DOT spends approximately \$10-12M/yr on the testing of soil and groundwater samples, which does not include the NYC-DOT. By moving the majority of these tests from an off-site analytical lab, to a field portable device the overall cost of construction budgets will be significantly lower and construction projects will experience fewer delays due to untimely analytical lab reports.

Semiconductor nanoparticles attract great interest for applications in materials science and nanotechnology^[1,2,3,4,5] due to the quantum confinement effect. These nanoparticles show special physical and chemical properties when their core size is close to or smaller

than the dimensions of the exciton Bohr radius of the material. Such unique properties of semiconductor nanoparticles, also known as quantum dots (QDs), have made them very promising for various practical applications including electronics, ^[6,7,8] optics, ^[9] chemical ^[10,11] and biological sensors. ^[1,12] A distinctive characteristic of these nanoparticles is that their photoluminescence (PL) properties have been shown to strongly depend on their surface environment. ^[13,14] Our interests are focused on developing QD-based sensing materials, which have the ability to provide multiple levels of selectivity through the tailored design of both the host matrix and the QD itself for a specified sensing application.

Chemicals

Technical grade (90%) trioctylphosphine oxide (TOPO), technical grade (90%) trioctylphosphine (TOP), cadmium oxide (99.99+%), anhydrous methanol (99.8%), anhydrous chloroform (99%), deuterated chloroform (99.8% atom D) were purchased from Aldrich. Selenium powder (99.9%) was purchased from Ventron. 1-hexadecylamine (HDA), benzoic acid (BA), stearic acid (SA), chloroform, methanol were purchased from Acros. Pentafluorobenzoic acid (FBA) was purchased from SynQuest Laboratories. Poly(methyl methacrylate) (PMMA) was purchased from Scientific Polymer Products, Inc. ethylene glycol dimethacrylate (98%), AIBN (2,2'-azo-bis(isobutyronitrile)), 2-naphthylamine (NA) were purchased from Aldrich. Selenium powder (99.9%) was purchased from Ventron. 1-hexadecylamine, benzoic acid (BA), stearic acid (SA), lauryl methacrylate (96%), chloroform, methanol were purchased from Acros. n-hexyl methacrylate was purchased from Scientific Polymer Products, Inc. Stearyl methacrylate was purchased from TCI America. Behenyl methacrylate was purchased from Monomer-Polymer & Dajac Labs, Inc. 1,6-hexamethylene diisocyanate (HMDIC) (99%), 3-aminopropyltriethoxysilane (APTES) (99%), methanol were purchased from Acros Organics. 11-Hydroxyundecanoic acid (11-HUDA) and 16-hydroxyhexadecanoic (16-HHDA) acids were purchased from Oakwood Products.

Synthesis and surface-functionalization of CdSe Quantum Dots

The CdSe quantum dots with stabilizing (TOPO and stearic acid, SA) and surface enhancing groups (choice of benzoic acid (BA), pentafluorobenzoic acid (FBA), 4-phenylbutanoic acid (PBA), 6-phenylhexanoic acid (PHA)) have been synthesized according to procedures modified from those previously published. In a typical reaction procedure CdO (0.103 g, 0.8 mmol) and stearic acid (0.911 g, 3 mmol) were placed into a three-neck flask and heated to 150°C under a dinitrogen flow for the synthesis of unmodified QDs, while the respective addition of benzoic acid (0.048 g, 0.4 mmol) or pentafluorobenzoic acid (0.085 g, 0.4 mmol) to this mixture was utilized for the synthesis of the surface modified QDs. After CdO was completely dissolved, the mixture was allowed to cool to room temperature and 6 g of TOPO and 3 g of HDA were added to the flask. The mixture was then heated to *ca.* 300°C under a dinitrogen flow. At this temperature a Se solution containing 0.632 g of Se powder in 4.2 mL of TOP was swiftly injected. After the injection, the temperature was reduced to 250°C. At the desired QD size, the reaction was stopped by removal of the heating bath. Aliquots were mixed with methanol and the precipitated QDs were separated by centrifugation. In order to remove

unbound reagents, the process of dispersion in methanol and centrifugation was repeated several times.

Sensing film development

The QDs, prepared as described above, have been encapsulated into PMMA matrices. Films of a micron-range thickness were prepared by drop coating a QD/PMMA solution onto Si-substrates, with the resulting droplet left to slowly evaporate in a covered dish overnight. The drop-coated films were observed to undergo a QD phase separation from the polymer matrix with an increase in QD loading of the polymer host. This is due to the limited miscibility of TOPO covered QDs within the PMMA matrix [15, 16, 17, 18, 19, 20, 21]. However, the non-uniformity did not significantly affect the hydrocarbon (HC) sensing characterization, as the optical properties of the QD films were collected and averaged over a 5 mm-diameter spot size. The reproducibility of producing QD-polymer films via the drop coating technique was addressed by depositing 15 individual QD-FBA/PMMA films from the solution, and comparing the PL for all 15 films. Furthermore, the xylenes sensing properties were measured for 5 of these films to examine the consistency of their detection characteristics. Arrays of these films were manually deposited using micro-pipette methods on silicon and anodized alumina substrates(AAO).

Characterization

Uv-vis absorption spectra were recorded on a Varian Cary Uv-vis spectrophotometer. The band gap energy was determined by analyzing the absorption data using the method outlined by Yu et al.. These values were then used to estimate the diameter of the QDs. Photoluminescence (PL) spectra of the QD solutions were acquired using a Varian Eclipse spectrofluorometer. High-resolution transmission electron micrographs were obtained on a JEOL 2010F transmission electron microscope (TEM) operating at 200 keV. The TEM samples were prepared by placing a dilute solution of QDs in chloroform onto carbon-coated copper grids and allowing them to dry in a vacuum desiccator overnight. High resolution TEM and X-ray diffraction data confirmed a high degree of crystallinity of the QDs. The QD diameters and size distributions determined through

^1H and ^{19}F NMR spectroscopy data were used to analyze the degree of attachment of the surface groups to the QDs. The purified QDs were dried in the dark for 2 hours under vacuum at 50°C to remove any remaining volatile organics. The QDs (0.020 g) with BA or FBA groups on the surface were then dissolved in 1 mL of CDCl_3 . ^{19}F NMR spectra were obtained using a Varian Gemini 300 MHz spectrometer. ^1H NMR spectra were obtained using a Bruker Avance 400 MHz spectrometer. Chemical shifts for ^1H NMR spectra are reported as parts per million relative to tetramethylsilane, while the ^{19}F NMR spectra are reported relative to CFCl_3 .

Hydrocarbon exposure testing

The sensing films were rigidly mounted in a stainless steel testing chamber with an internal volume of 20 cc. A Varian Eclipse spectrofluorometer was employed to characterize the PL properties of the sensing films. The spectrometer utilized a bifurcated fiber optic accessory for both delivery of the 350 nm excitation light to the film surface, via a vacuum compatible fitting, and collection of the resulting emission for detection. A

HC vapor producing system using a glass bubbler and an Environics gas mixing system generated HC vapor concentrations adjustable from several ppm to several percent by changing the gas flow through the bubbler. The total pressure of the bubbler was monitored and maintained at 850 torr, while the bubbler was under ambient room temperature conditions. Thermal measurements of the bubbler during the experiments indicated that the temperature fluctuated by $\sim 1^\circ\text{C}$, and thus the toluene and xylenes concentrations delivered to the testing station only varied by $\sim 3\text{-}5\%$ throughout the testing period. The HC sensing capabilities of the films were characterized by monitoring the peak PL intensity change of the QDs while the gas environment of the test chamber was varied from pure N_2 to a HC/ N_2 mixture through the computer controlled vapor-producing system, with 5 minute half cycles used for each exposure test. The total test gas flow, pressure and temperature within the testing chamber were maintained at 1200 sccm, 760 Torr and $\sim 25^\circ\text{C}$, respectively.

Array Studies

In Figures, 1, 2 and 3 for the array study on the Ocean Optics spectrometer, fluorescence spectra of the QD films deposited on AAO show a peak at longer wavelengths, $>500\text{ nm}$ characteristic of QD emission. Shown in Figure 2 are 3 film arrays tested for reproducibility. Peak photoluminescence intensity is recorded for all films before exposure to HCs so that it can be monitored as a function of time and xylenes concentration. In Figure 1 it is seen that an array of 3 individual QDs from QD NA 1 samples were deposited successfully where, the three distinct wavelengths of 520nm, 555nm and 595nm are separated and are of comparable intensity. The Ocean Optics spectrometer, however, could not distinguish between the QD NA 2 595nm QD and the QD NA 2 607nm QD since their size separation was not large enough. As a result, and is shown in Figure 2, only 2 of the 3 QD NA 2 samples were deposited as films, with their respective peak emission wavelengths at 555nm and 607nm. There is good reproducibility seen between the 3 separate arrays that were made as seen in Figure 2. Figure 3 shows that 3 distinct Evident QDs with wavelengths of 505nm, 570nm and 616nm were deposited as an array with varying PL intensities, which can be attributed to the difference in the concentration of the QD solutions.

QD NA 1 Array Ocean Before Exposure

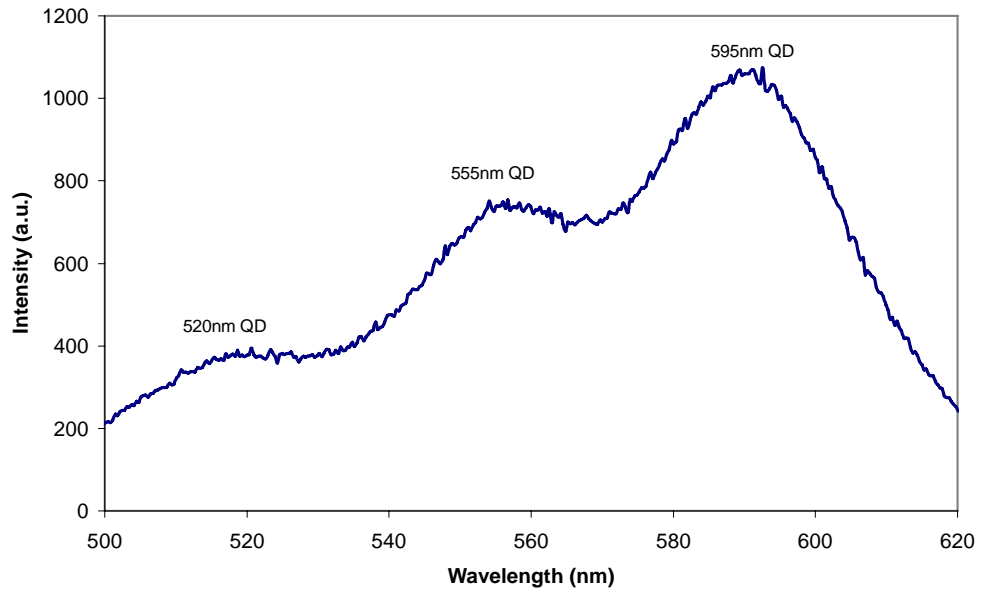


Figure 1 Ocean Optics fluorescence data for QD NA 1 films on AAO

QD NA 2 Array Films Before Hydrocarbon Exposure

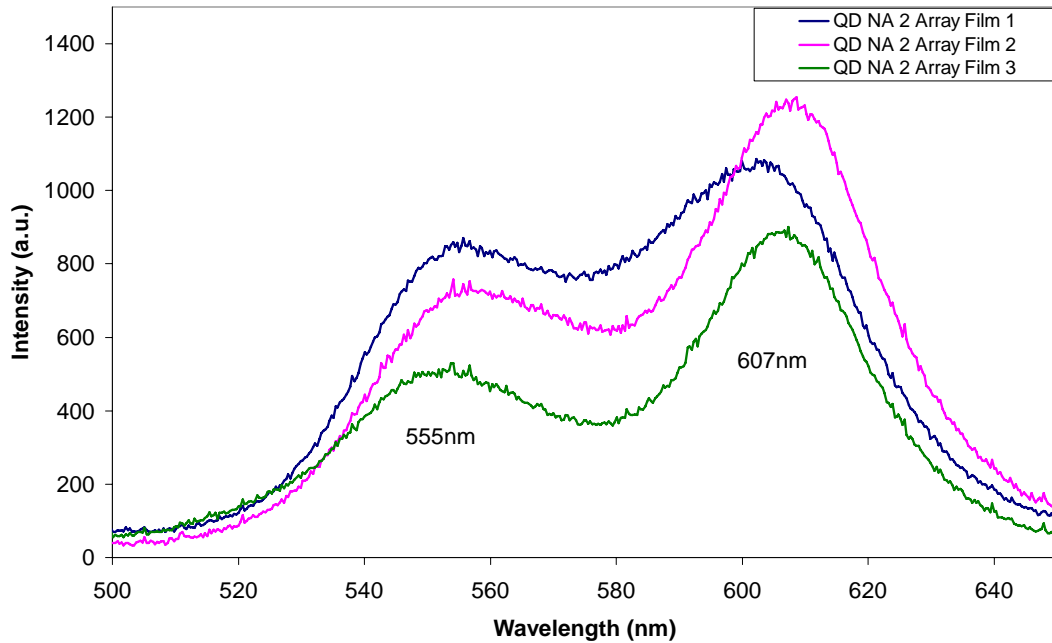


Figure 2 Ocean Optics fluorescence data for QD NA 2 films on AAO

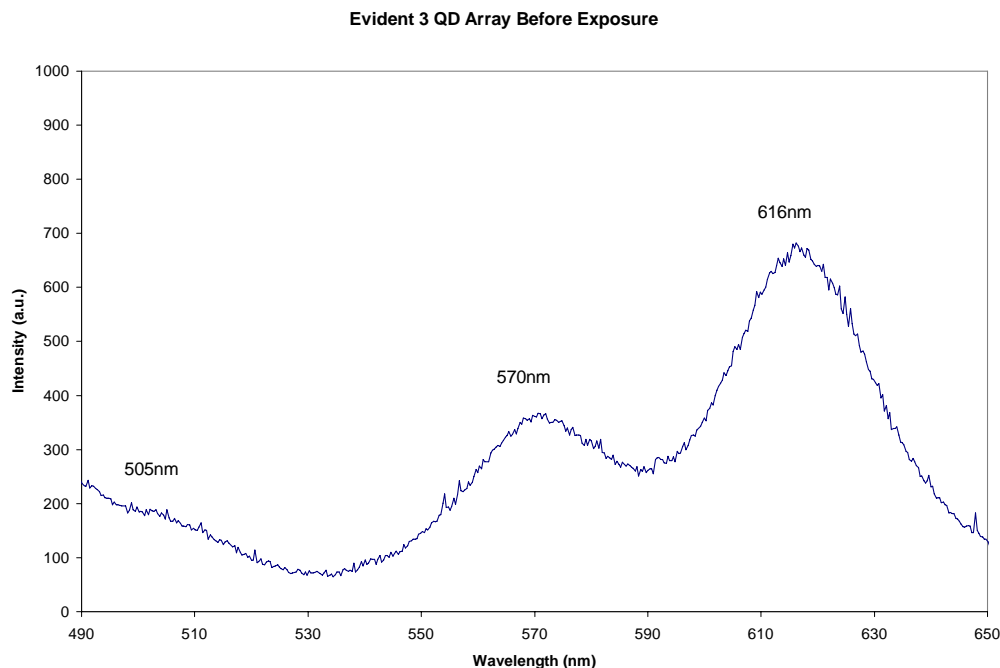


Figure 3 Ocean Optics fluorescence data for Evident QDs films on AAO

Ocean Optics Sensing Array Data

Prior to the HC exposures the QDs on AAO films were photocured under 380 nm irradiation and a 1200 sccm flow of air until a stabilized peak PL baseline was established, generally this takes about 30 minutes. The films are then exposed to 2 repeating cycles of gas-on and gas-off for increasing concentrations of xylenes from 15-9400ppm in air. Figure 4 illustrates a standard sensing curve for QD NA 1 films on the Ocean Optics spectrometer.

While we were successful in creating a 3 QD array with good separation of the individual QD's, the QD NA 1 films did not have the typical response to the hydrocarbon exposure cycles as seen in the films from the previous chapter. Specifically, at all concentrations we see inversion of the PL signal and rather than an increase, the PL intensity actually decreases. We have seen this effect in previous studies and define it as PL quenching. It is related to a reversible change in the physical integrity of the film and its corresponding wetting properties at characteristic HC concentrations. The PL quenching effect tends to compete with PL enhancement and the competition between the two sensing mechanisms desensitizes the sensor when the PL enhancement and PL quenching essentially cancel out at a characteristic HC exposure.²² Films that are thicker and are observed to be non-homogenous tend to show inversion when exposed to HCs. Conversely films that are uniform and thin tend to show PL enhancement and are not as susceptible to this competing effect.²³ The QD NA 1 films for this study were visibly

non-homogeneous and it is believed that this is why they did not show good sensing characteristics. While the QD NA 1 solutions worked well for the previously described

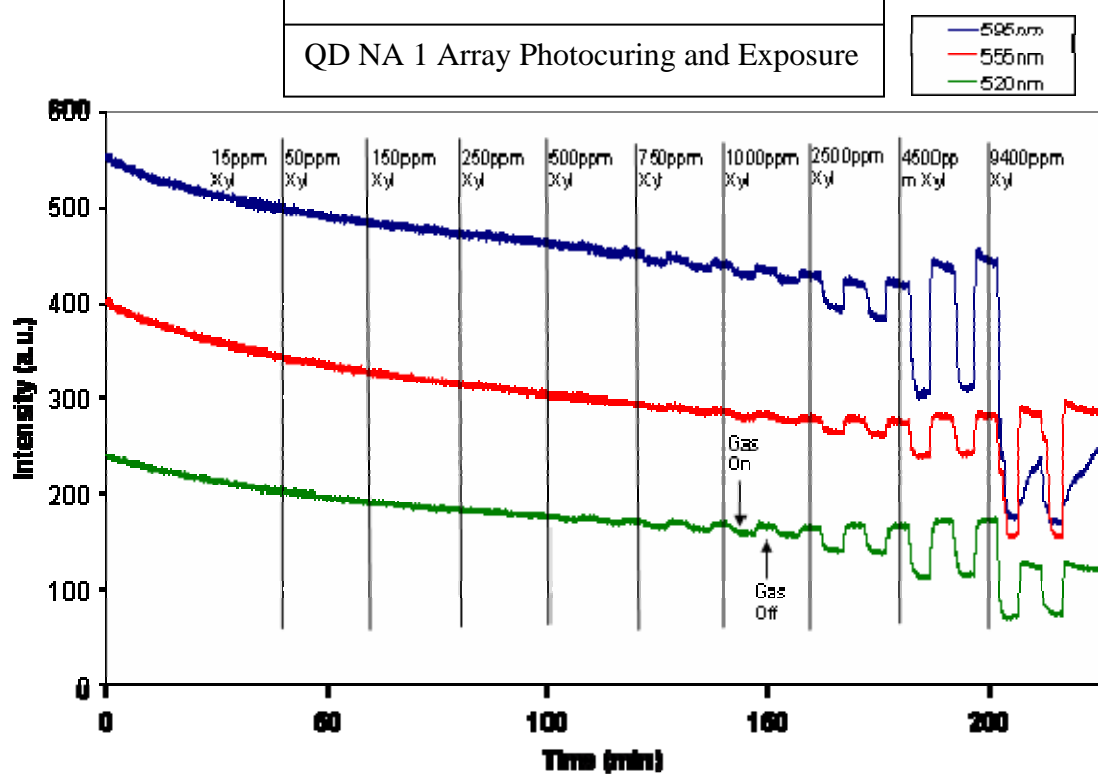


Figure 4 Ocean Optics sensing curve for QD NA 1 array 15-9400ppm xylene

ligand coverage study it is likely that since it was an aged sample, ~2 months, it did not perform well for the subsequent array study.

Therefore, to continue the array study, films of the QD NA 2 were deposited on AAO and analyzed. Figure 5 shows the sensing curve for the QD NA 2 array. It is clear that the surface modified QDs showed a response towards xylenes as seen through the increase in photoluminescence as the concentration of the hydrocarbon increases. Average response times to the different concentrations of xylenes were 15-20 seconds and the average recovery time was also 15-20 seconds. At the highest exposure of 9400ppm xylenes, the 555nm QD shows slight inversion of the PL signal and quenching.

Baseline subtraction curves were performed in the mathematical program Origin as described in the previous chapter and are shown in Figures 6 and 7. From the baseline subtraction the change in intensity for each cycle of gas on was calculated and the average and error was determined for all concentrations. To investigate the reproducibility, 3 sets of QD NA 2 arrays were made and tested as a function of their photoluminescence change to hydrocarbons. The three films for each sample were averaged and plotted in a calibration curve seen in Figure 8 and 9 for concentrations below 1000ppm. We are able to see detection limits as low as 15ppm. We attribute this lower detection limit on the Ocean Optics spectrometer to better and fresher solutions of QDs. In the previous chapter with the ligand coverage study we only saw detection limits

of 250ppm, this may have been due to the fact that the QD solutions had aged and were susceptible to some oxidation, and is not due to the sensitivity limitations of the Ocean Optics spectrometer with respect to the Varian spectrometer. The standard deviation for the change in intensity of the 3 runs is relatively low, ~1.5 at

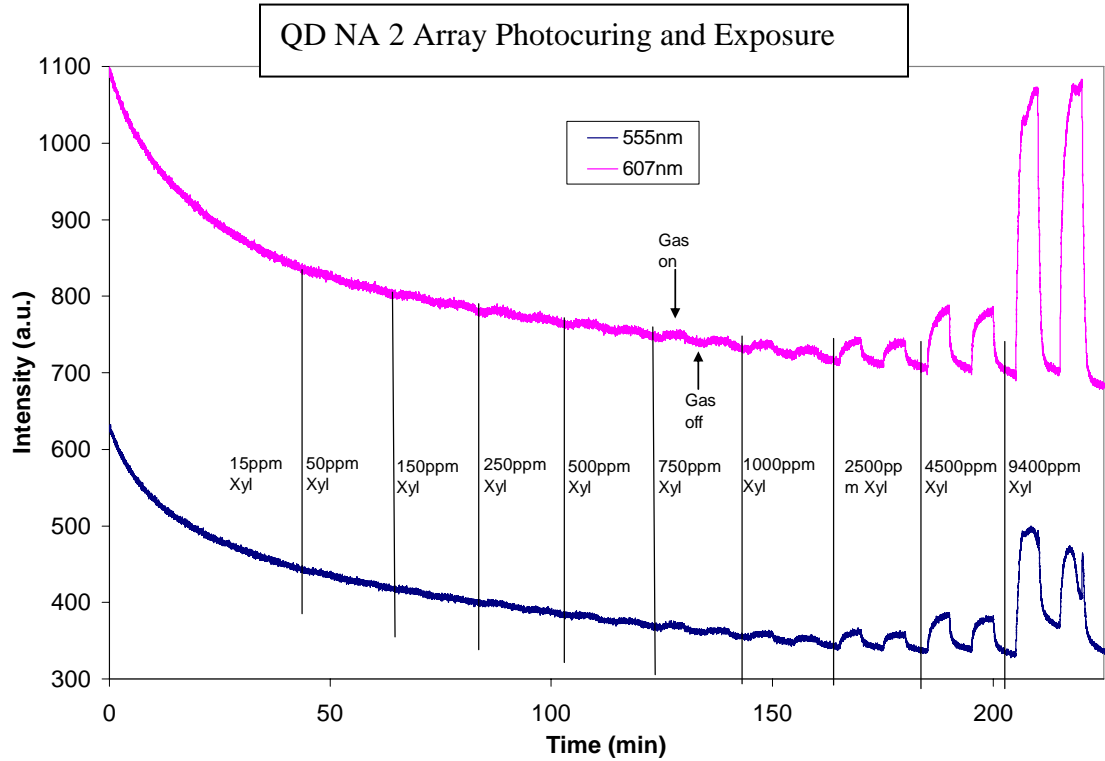


Figure 5 Ocean Optics sensing curve for QD NA 2 array 15-9400ppm xylene

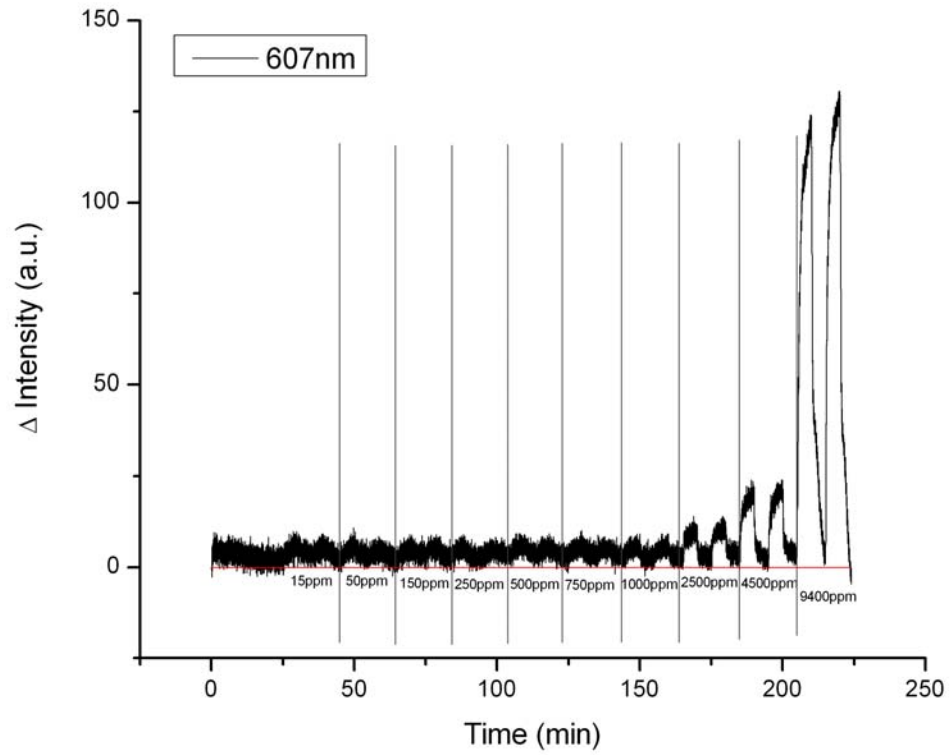


Figure 6 Baseline subtraction for QD NA 2 607nm

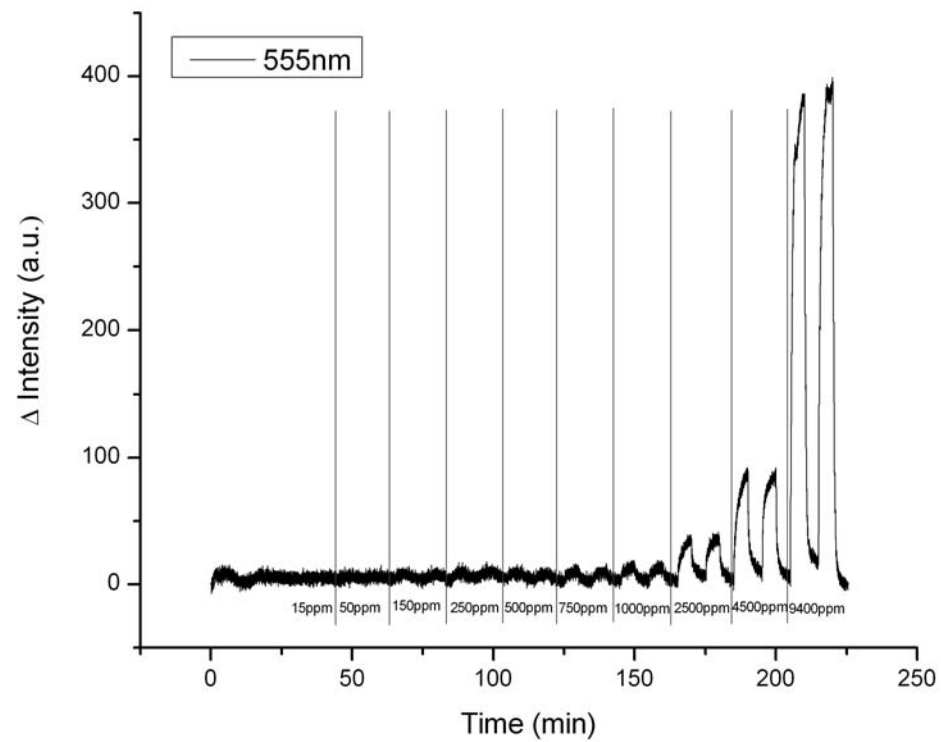


Figure 7 Baseline subtraction for QD NA 2 555nm

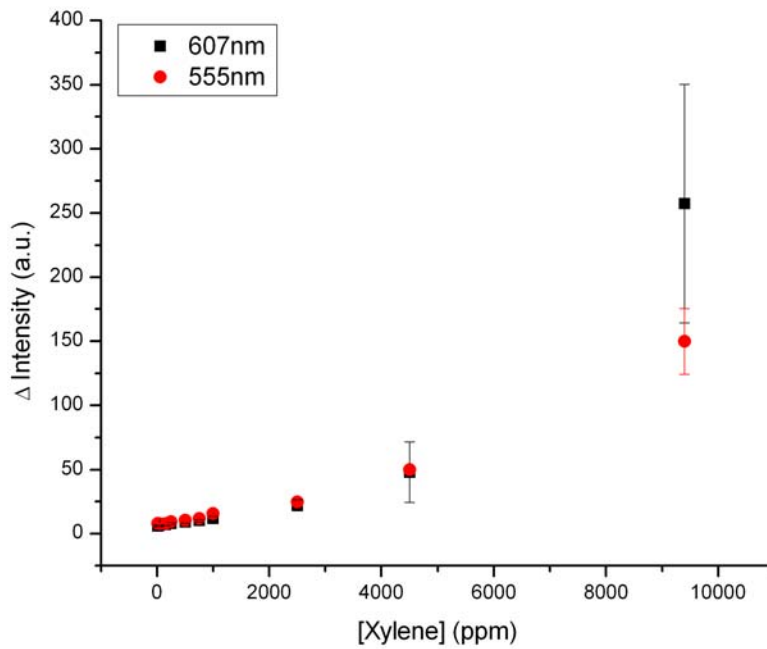


Figure 8 Average of three calibration curves for QD NA 2

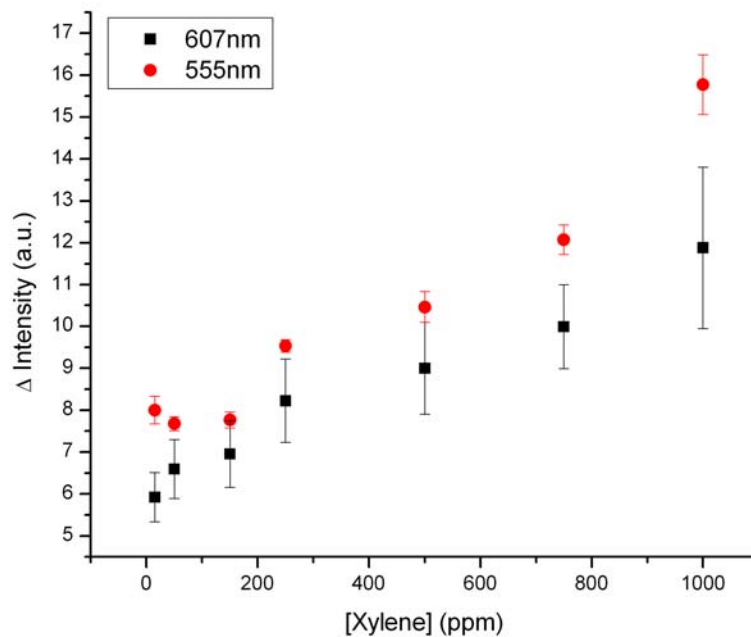


Figure 9 Average of three calibration curves for QD NA 2 at low HC concentrations
 HC concentrations below 1000ppm and ~7.8 at concentrations above 1000ppm, which shows that QD films have good reproducibility.

The commercially available QDs from Evident Technologies were used to obtain better QD size separation and also to serve as a comparison to the QD-NA dots used for

these studies. With better QD size separation we should be able to make arrays with more elements, which would likely enable better selectivity studies in our future work. To continue the array study, films of the Evident QDs were deposited on AAO and analyzed. Figure 10 shows the sensing curve for the Evident QD array. Baseline subtraction analysis was performed on this plot and calibration curves were made as seen in Figures 11, where exposures range from 15-9400ppm. For the commercially available QDs there was only a detection limit as low as 750ppm for xylenes. These are very preliminary results and from the liquid fluorescence data we know that the concentrations of these Evident QD solutions are different so we can not make any conclusions about how the size of the QD affects the sensing properties. Also since these are commercially available QDs we do not know all of the ligands that are on the QD, we believe that there are stabilizing ligands such as TOPO. This could account for the fact that these QDs were not as sensitive to the HCs as our QDs that were synthesized with surface enhancing ligands.

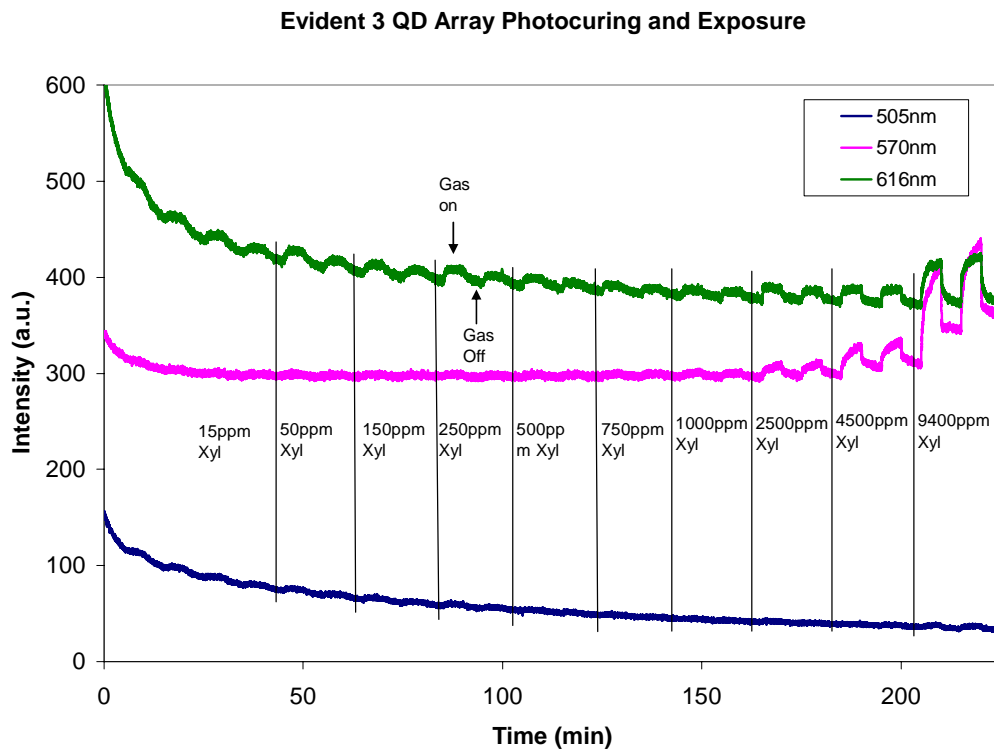


Figure 10 Sensing curve for Evident 3 QD array

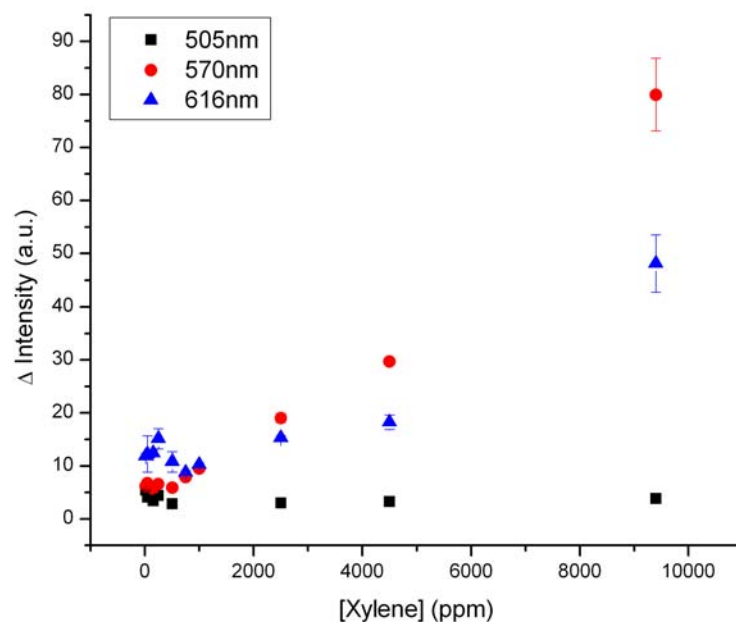


Figure 11 Evident 3 QD array calibration curve

In summary these array studies, though preliminary, did show that we are able to create multiple element arrays and observe sensing for each individual element simultaneously. The ability to create and study these arrays are promising results. Furthermore, we have shown that with fresh QDs the smaller more cost effective Ocean Optics spectrometer is capable of being sensitive at ppm concentrations similar to that of the larger and more expensive Varian spectrometer. Likewise, the use of these sensing arrays will allow us to collect more data faster and by tailoring arrays to specific targets we can eventually achieve higher degrees of selectivity in our hydrocarbon measurements. However, it became readily apparent that the CdSe quantum dots used in these studies, suffer from an inherent instability in their baseline photoluminescence, and furthermore, suffer from reliability issues with regards to reliable batch to batch synthesis of the same sized quantum dot with the same baseline photoluminescence. The array portion of the program suffered from several months of poor quality quantum dots and thus these studies did not progress as quickly as planned. Initial array studies using capped quantum dots, CdSe-ZnS, indicated that they were far more stable as a function of time due to their ruggedness against oxidation however these films required optimization to ensure their viability for repeatable detection over the full 15-9400ppm sensing range.

CdSe-ZnS Quantum Dot Study

The detailed results of this work are being drafted into a manuscript to be submitted to Applied Physics Journal. However, in summary through a combination of proper substrate and CdSe-ZnS QD choice we have been able to test the reliability and stability

of these films and over an 8 month period of time they showed remarkable characteristics. Over a period of 252 days these samples displayed only a 10nm blue shift in the peak photoluminescence (PL) for these QDs with a minimal decrease in the overall PL intensity. Such a stability is an indication of a nearly 8month long stability lifetime of these CdSe-ZnS QD sensing materials, which is in stark contrast to the days-long lifetime, which is typical of CdSe uncapped QDs when exposed to air without any polymer protection. Very encouraging is that the sensing performance of the sample is not impacted as revealed in Fig. 12, where the difference between the seemingly two groups of curves may result from the sample mounting.

These results have been critical to obtain to prove the stability of this material in a sensing environment. Future studies will be aimed at increasing the hydrocarbon sensitivity to the ppb range.

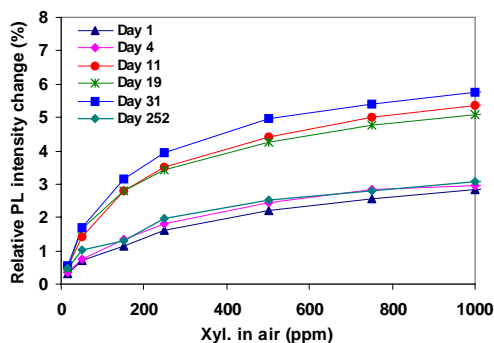


Fig. 12 Xylenes sensing performances of an AAO/QD (core/shell) sample over a time period of 252 days

Quantum Dot-Ligand Distance Dependence Study

Quantum dots based hydrocarbon detection through the use of on an energy transfer mechanism will require a distance dependence study for the proposed ligands in these studies. From our previous work it appears clear that electrostatic interactions between the hydrocarbon targets and the surface ligands dominates the optical response of the tailored quantum dots. Therefore, by studying the surface ligand length dependence on the overall sensing response of the quantum dots, one can further characterize this sensing response and optimize the surface ligands appropriately. A detailed study was performed and the results of this study have been submitted for publication in the Journal of Physical Chemistry C.

A new sensing material fabricated by the technique we developed to integrate colloidal CdSe QDs on quasi photonic crystal (PC) anodic aluminum oxide (AAO) platform enables monotonic PL response to HC exposures over three orders of magnitude. Based on this new sample structure, we conducted a study on the hydrocarbon sensing properties of CdSe QDs tailored with phenyl group carrying surface enhancement agents to determine the sensing dependence on the aromatic group distance from the QD surface. This work is

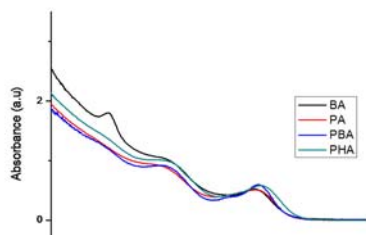


Fig.13. The absorbance spectra of CdSe QD solutions with same QD size and concentration.

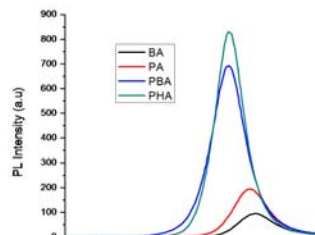


Fig. 14. The photoluminescence spectra of CdSe QD solutions in chloroform with same QD size

expected to help develop a better understanding of the underlying sensing mechanisms along with methods for achieving the desired sensitivity, selectivity and reliability of QD-based chemical sensors.

Fig. 13 shows similar UV-Vis absorbance spectra of four solutions of CdSe QDs capped with TOPO, SA and HDA as stabilizing agents but different acids as surface enhancement agents, namely, benzoic, phenylacetic, phenylbutanoic or phenylhexanoic acids (BA, PA, PBA, PHA). According to the data (see Table 1) calculated from Fig. 13, the QDs in the four solutions have close sizes, extinction coefficients, and concentrations, which is important for sensing comparison in this study, although there are slight increases in these values with changing the surface group from BA to PHA. Unexpected is that PL from QDs bound with PHA or PBA is much stronger than that with PA and BA (Fig. 14), which is in good agreement with the measured quantum yields (QY) listed in Table 1. The proportional correlation of quantum yield or PL with an increasing distance between the phenyl ring of the surface enhancing ligand and the QD surface may be an

Table 1. QD Size (nm), Extinction Coefficient ($\text{cm}^{-1} \cdot \text{M}^{-1}$), Quantum Yield and QD solution molar

Sample	QD (nm)	Size	Extinction Coefficient ($\text{cm}^{-1} \cdot \text{M}^{-1}$)	QD (M)	Concentration	Quantum Yield (%)
BA	3.4		154166	5.1E-06		4.5
PA	3.5		160676	4.7E-06		10.6
PBA	3.5		167574	4.8E-06		28.3
PHA	3.6		178705	4.9E-06		29.4

indication of charge transfer effect between them as detailed below.

For this study, it is important to identify the surface coverages of the above surface bound agents to make sure they have similar values as different coverages will likely affect the degree of ligand to QD charge transfer effects. NMR is a powerful technique and capable for this analysis. As an example, Fig. 15 reveals chemical shift and broadening of ^1H NMR spectra QD-bound PA

ligands in chloroform compared to free PA in chloroform, proving that PA is indeed bound to the QD surface. Based on integration analysis of the NMR peaks for the nanoparticle samples, surface ligand molar values normalized to the surface-enhancing agent together with the normalized chemical reagent information used for the nanoparticle syntheses is given in Table 2. Moreover, by mixing the same amount of each QD (BA, PBA and PHA) separately with a QD-PA sample, the exact enhancing ligand ratios relative to PA were measured as 0.93, 0.95, and 1.13 for BA, PBA and PHA, respectively. Through this integration it can be seen that the ratio of surface

Table 2. Normalized mole ratios of various surface ligands of CdSe QDs with respect to surface enhancing agent determined by ^1H NMR along with synthesis values

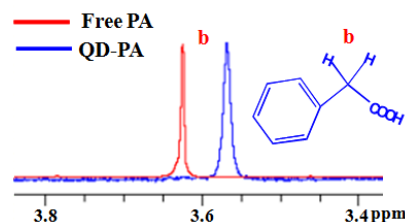


Fig. 15 Comparison of the singlet peak (b) in ^1H NMR spectra of free PA vs. bound PA to surface of QD.

Sample	Ligand	HDA	SA	TOPSe	TOPO
BA	1	15.4	NA	9.5	25.5
PA	1	13	5.5	9	23
PBA	1	14	NA	9	23
PHA	1	13	5	8.5	23
synthesis	1	15.5	4	10	21.2

enhancing ligand to the surface stabilizing ligands is essentially the same for the QD-BA, -PA, -PBA and -PHA samples, which is consistent with quite similar values expected from the reagent synthesis information. Moreover, since the ligand ratios of the QD-BA, -PBA and -PHA samples with respect to the QD -PA sample, are all approximately equal to 1, we can conclude that each of the QD samples used in this study have very similar ligand coverages, which is a critical point to verify prior to studying the hydrocarbon sensing results.

Thus, according to the studies presented in the literature, the cause of the observed decrease in quantum yield as a function of the phenyl ring to QD surface distance may result from charge transfer between the surface agent and the CdSe QD when they have similar surface coverage. The charge transfer seems more efficient for smaller BA bound QDs relative to the other surface enhancing ligands modified QDs. Therefore, it is not unexpected that when the aromatic ring gets further away from the QD surface in PBA and PHA ligand the quenching effect decreases and the PL intensity increases drastically. Other possible explanation for the lower quantum yield observed for the smaller ligand bound QD samples may pertain to possible accelerated growth of particles. Also it could be associated with the ligand length itself and its overall affect on surface passivation.

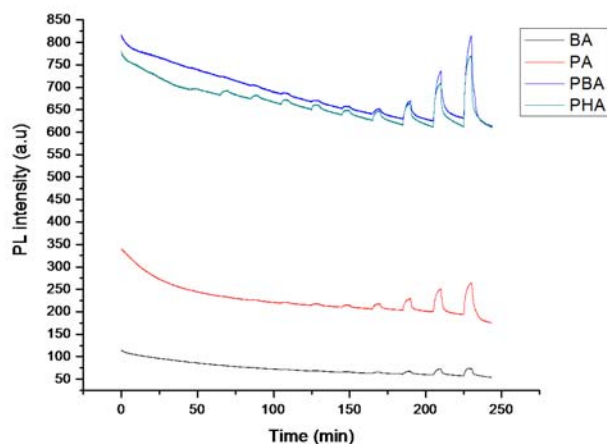


Fig.16 Gas on/off curves for four QD films on AAO substrate upon exposure to various concentrations of xylenes.

Four QD films cast on AAO supports from the four solutions show consistent PL spectra pattern with that presented in Fig. 14 for QD solutions. Their sensing traces depicted in Fig.16 demonstrate PL enhancements upon exposure to xylenes in air over all the concentration range without PL quenching effect observed, though the Y-scale is too large to allow sensing traces at low analyte levels distinguishable. As understood

previously, the PL enhancement upon HC exposure is believed to arise from passivation of non-radiative surface states of the QDs.

From Fig. 16, sensing characteristics of absolute and relative or normalized PL changes as a function of xylenes concentration, calculated after subtraction of decreasing baseline, are compared in Fig. 17 and 18, respectively. Interesting is that the sensing performances of the QDs with PHA and PBA toward xylenes exposure are larger than those with PA and BA, analogs to their PL relation trend shown in Fig. 17. Their sensitivity values in Table 3 reported in two regions, below 2500 and above 4500 ppm xylenes indeed exhibit the same trend, i.e., the sensitivity values towards xylenes increases with the surface enhancing ligand length getting longer. However, upon inspection of Figure 18 it is apparent that the normalized PL changes in all four samples are approximately the same, suggesting the same sensing characteristics and mechanism pertain for all four samples.

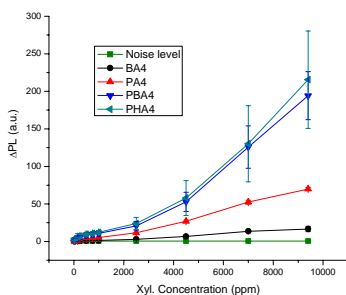


Fig.17 Absolute change in PL upon QD films exposure to Xylenes vs. HC concentration.

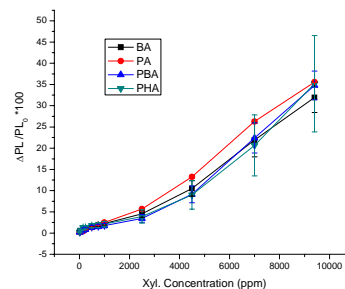


Fig.18 Normalized change in PL upon QD films exposure to Xylenes vs. HC concentration.

In summary, a higher quantum yield or PL from the QDs with the longest surface enhancing ligand, PHA, makes it more sensitive towards xylenes detection and a better candidate in designing the aromatic hydrocarbon optical sensors for this method. As discussed above, this is likely resulting from better surface state passivation effects with the longest ligand, producing the greatest signal change upon hydrocarbon exposure.

In summary, a higher quantum yield or PL from the QDs with the longest surface enhancing ligand, PHA, makes it more sensitive towards xylenes detection and a better candidate in designing the aromatic hydrocarbon optical sensors for this method. As discussed above, this is likely resulting from better surface state passivation effects with the longest ligand, producing the greatest signal change upon hydrocarbon exposure.

Table 3. Sensitivity values at low concentrations (below 2500 ppm) and high concentration (above 4500 ppm) of Xylenes.

Sample	Sensitivity toward Xyl. (15-2500 ppm) * 10 ³	Sensitivity toward Xyl. (4500-9400 ppm) * 10 ³
BA	1.0	2.0
PA	4.5	8.8
PBA	7.4	28.8
PHA	8.2	32.1

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